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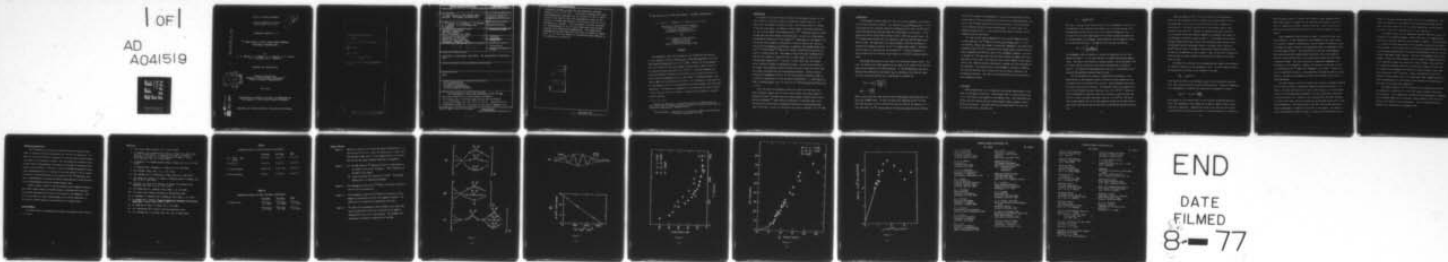
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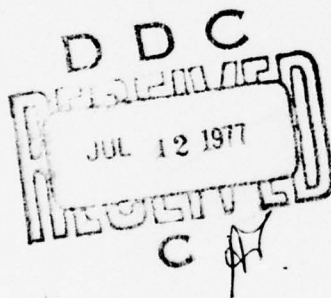
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³¹P NMR STUDIES OF THE LINEAR CHAIN MAGNETS:
POLY(METAL PHOSPHINATES)

by

L. S. Smith, P. R. Newman, A. J. Heeger, A. F. Garito,
H. D. Gillman, and P. Nannelli

Prepared for publication



Pennwalt Corporation
Research and Development Department
King of Prussia, Pennsylvania ✓

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^{31}P NMR STUDIES OF THE LINEAR CHAIN MAGNETS: POLY(METAL PHOSPHINATES)[†]

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ABSTRACT

The paramagnetic shift and linewidth of the ^{31}P NMR have been measured for three magnetic polymers $\text{Co}[\text{OP}(\text{C}_4\text{H}_9)_2\text{O}]_2$, $\text{Cr}[\text{OP}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_2\text{OH}$, and $\text{Cr}[\text{OP}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_2[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]$ for $77\text{K} \leq T \leq 300\text{K}$. Analysis of the paramagnetic shift as a function of the static magnetic susceptibility yields a value for the hyperfine coupling constant $A \approx 4 \times 10^{-4} \text{ cm}^{-1}$. Previously measured and calculated hyperfine constants for an electron in the 3s and 3p orbitals are used to show the paramagnetic shift is due mainly to transferred magnetic spin density ($\approx 0.1\%$) in the phosphorus 3s orbital. The linewidths of these materials are approximately 10 Oe at room temperature and broaden slightly with decreasing temperature. The temperature dependences of the linewidths are used to deduce an upper limit ($\leq 1\%$) for the amount of transferred spin density in the phosphorus 3p orbital.

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INTRODUCTION:

The family of polymers known as poly(metal phosphinates) consists of metal ions linked in a chain-like fashion by phosphinate bridges, (Fig. 1). The metal ion in the magnetic polymers is either a 3d-transition metal or a member of the rare earth group. In addition, various organic side groups (denoted R', R'', etc.) can be bonded to the phosphorus atom.^{2,3,4} Systematic material science studies show that these organic side groups play a crucial role in determining the mechanical properties of each compound.^{5,6} Measurements of the magnetic susceptibility and the magnetic contribution to the heat capacity are consistent with an anti-ferromagnetic superexchange of magnitude $1K \leq |J/k| \leq 30K$ between metal ions.^{7,8} X-ray studies^{9,10} indicate the distance between metal ions along the chain is typically about 5\AA . Thus magnetic dipolar and direct exchange mechanisms will not produce an interaction that is large enough to account for the observed Weiss temperatures.¹¹ Instead it is more likely that the exchange occurs indirectly through the phosphinate bridges. Located at the midpoint of the bridge, the phosphorus nucleus is ideally situated to probe the delocalized spin density associated with the superexchange mechanism. We have therefore measured the paramagnetic shift of the ^{31}P Nuclear Magnetic Resonance (NMR) as a function of temperature in three poly(metal phosphinates): 1) $\text{Co}[\text{OP}(\text{C}_4\text{H}_9)_2\text{O}]_2$, CDBP 2) $\text{Cr}[\text{OP}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_2\text{OH}$, Cr A-type and 3) $\text{Cr}[\text{OP}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_2[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]$, Cr C-type.

X-ray and optical birefringence studies have shown the Cr A-type to be mostly amorphous, whereas the Cr C-type is more regular with chain lengths of hundreds of units.⁸ The CDBP forms well ordered single crystals whose structure has been determined.¹⁰ These relative differences in structural order can be associated with proportionally broadened distributions of superexchange magnitudes¹¹ which may, in turn, be reflected in the spectral linewidth of the ^{31}P NMR.

EXPERIMENTAL:

Several grams of powder samples of each of the three materials was prepared by the method described elsewhere. The copolymer $Zn_{1-x}Co_x[OP(C_8H_{17})_2O]_2$, $x \approx 0.01$, was precipitated by combining 0.0200 mole $K[OP(C_8H_{17})_2O]$ in 50 ml. of 95% ethanol with 0.0099 mole $ZnSO_4 \cdot 7H_2O$ and 0.0001 mole $CoSO_4 \cdot 7H_2O$ in 50 ml of H_2O . It was washed with 100 ml of H_2O before drying in vacuo at $60^\circ C$ for several hours. The ^{31}P resonance was observed over the temperature range from 300-77K using pulsed NMR at 10 MHz. The magnitude of the applied magnetic field was determined by observing the resonant frequency of free 1H in $MnBr_2$ -doped ethanol. Phosphoric acid was used as a reference for the unshifted ^{31}P . A boxcar integrator was used to sample the free induction decay signal as a function of applied magnetic field.

Pulsed NMR spectroscopy is most useful for determining resonant fields. However, the width of the signal observed at the output of the boxcar is not directly equal to the linewidth of the NMR absorption. If the NMR absorption spectrum is Gaussian with half-width at half-power $\Delta H_{\frac{1}{2}}$, the envelope of the observed signal (see Fig. 2) is also Gaussian and is approximately described by:

$$f(H) \propto \exp \left[- \frac{(H-H_o)^2}{C(\Delta H_{\frac{1}{2}})^2} \right]$$

$$\text{with } C = \frac{t_1+t_2}{t_2-t_1}$$

where t_1 and t_2 are the times when the boxcar sampling gate opens and closes and H_o is the resonant field. In order to extract the linewidth of the ^{31}P resonance from the data, we first recorded (The spectral width of the sampling r.f. is less than 4kHz.) the ^{31}P spectrum and the 1H spectrum using the pulsed technique.

Since the ^1H resonance was approximately 1.6 Oe wide and relatively intense, we were able to record the absorption spectrum directly using CW methods. The width of the ^1H signal measured by the pulsed technique (~ 7 Oe) was divided by the linewidth obtained from the CW measurement (~ 1.6 Oe) to derive the apparatus scaling factor, C. This factor was then used to calculate the ^{31}P linewidth from our pulsed data.

As a test of the relative magnitude of the so called "chemical" shifts in these materials, the ^{31}P NMR in poly- $\{\text{Zn}_{1-x}\text{Co}_x[\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}]_2\}$, $x \approx 0.01$, was observed. Because this sample is essentially diamagnetic, the spin-lattice relaxation time of the ^{31}P is relatively long, making signal recovery with the boxcar integrator more difficult than for the paramagnetic samples. An effort to increase T_1^{-1} and narrow the line was made by mixing the sample with tetrahydrofuran to form a gel. This produced a more intense signal of width approximately 2 Oe, hopefully without substantially changing the local environment of the phosphorus. The chemical shift in this diamagnetic material at 300K was less than one oerstead, which is much less than the shifts observed in the paramagnetic materials. Thus none of the measured shift can be attributed to such diamagnetic effects.

DISCUSSION:

Induced magnetization on a non-magnetic atom through superexchange is well known in many magnetic materials. Superexchange leads to a partial delocalization of spin density from magnetic to non magnetic ions. This transferred spin density may then interact with the nuclear magnetic moment through a contact hyperfine interaction. The usual effective spin Hamiltonian¹² for this type of nuclear-electronic interaction is:

$$H = -g_N \mu_N \vec{I} \cdot \vec{H} - A \vec{I} \cdot \vec{S}$$

where g_N , I , and μ_N are the nuclear g value, spin, and magneton, respectively. The magnitude of the transferred spin density at a particular nucleus can be experimentally derived from the size of the observed paramagnetic shift. If we replace \vec{S} in the above Hamiltonian by its thermal average and assume that the system behaves as a paramagnet (high temperature and low magnetic fields), we can show that the shift of the NMR from the free value is given by:

$$\Delta H = H_0 \left[\frac{A \chi}{g_N g_e \mu_N \mu_B N_0} \right]$$

The paramagnetic shift is shown as a function of temperature for all three samples in Figure 3. In all cases the shift is toward lower applied magnetic fields. The value of the hyperfine coupling constant A can be determined from the slope of ΔH as a function of the static susceptibility χ as shown in Figure 4. For relatively high temperatures, the plot is approximately linear and gives the hyperfine constants shown in Table I.

Use of this model of a partially transferred spin producing a local magnetization at the phosphorus permits the amount of spin transferred from the magnetic ion to be inferred from the data. Atomic phosphorus has valence electrons in the 3s and 3p orbitals. The hyperfine field of an unpaired electron in the 3s orbital has been calculated to be 3.2×10^6 Oe.¹³ Christian-¹⁴ has measured the hyperfine field for an electron in the 3p orbital and found it to have an average (isotropic) value of -1.4×10^4 Oe. The latter value is much smaller than the 3s (and negative) because the 3p wave function has a node at the nucleus and the interaction arises mainly from core polarization.

Using the magnitude only of the above theoretical and experimental values for the 3p hyperfine field, we deduce that several tenths of an electron would have to be present in the phosphorus 3p orbit to produce the observed shift. This much delocalization is unacceptably large in these relatively ionic materials. However, the magnitude and sign of the shift can be produced by much more moderate amounts of transferred spin density in the phosphorus 3s orbital as shown in Table I. If we assume that the superexchange between metal atoms involves the traditional partial electron transfer mechanism from the phosphinate bridge to the metal, then it has been shown¹⁵ that the shift of the NMR to lower applied fields is consistent with the sign of the hyperfine to the 3s orbital. Thus, we are led to conclude the observed shift is caused primarily by transferred spin density in the phosphorus 3s orbit.

The amount of 3p character in the transferred spin density will determine the amount of anisotropy in the paramagnetic shift. In these powdered samples, the anisotropy is reflected by the linewidth of the NMR:

$$\Delta H_{\frac{1}{2}} \sim H_{hf}(3p) \chi$$

where $\Delta H_{\frac{1}{2}}$ is the width at half-maximum, $H_{hf}(ep)$ is the anisotropic hyperfine field, and χ is the isotropic electronic susceptibility. Using the paramagnetic shift measurements to eliminate the susceptibility dependence, we obtain:

$$H_{hf}(3p) = H_{hf}(3s) \frac{d(\Delta H)}{d(\Delta H_{\frac{1}{2}})}$$

where $H_{hf}(3s)$ is the observed value for the isotropic transferred hyperfine field. The linewidth at room temperature is shown in Table II and is nearly temperature independent. Comparing this field to the value for the 3p field from Christensen's data gives the amount of transferred spin on the phosphorus,

which is given in Table I. However, this estimate is most certainly only an upper limit because it assumes that the transferred spin density is the only source of temperature dependent linewidth broadening. Hence, the presence of additional broadening mechanisms would serve to reduce the amount of 3p spin density.

Closer examination shows the data in Figure 3 to have two rather interesting features. At high temperatures, the paramagnetic shift, when plotted as a function of magnetic susceptibility, does not appear to extrapolate linearly through the origin, whereas at low temperatures there is considerable deviation from linear behavior. This contradicts the idea that the paramagnetic shift and the electronic susceptibility should both tend to zero together. Instead a linear extrapolation to zero susceptibility gives an upfield shift of several oersteds. This could arise from a temperature independent spin polarization on the phosphorus. However, the existence of this type of shift is contradicted by the ^{31}P NMR in the diamagnetic zinc isomer. In this material, the unshifted resonance at room temperature indicates the absence of spin density. The shift in the magnetic materials must therefore tend to zero at high temperatures.

The shift versus χ plots can be understood in terms of a slightly modified model in which we assume a temperature dependent hyperfine interaction. In Figure 5, we replot the data for Cr C-type as $\Delta H/\chi$ versus χ . If the hyperfine constant "A" were temperature-independent, this plot would give a horizontal line with the value "A". Instead, at low susceptibility, the shift increases at a faster rate than χ and then flattens out and decreases slowly with increasing susceptibility. Any extrapolation of the low χ part of the curve may be used to approximate the behavior of the shift in this region. For example, a linear extrapolation as shown in Figure 5, results in the solid line shown in

Figure 4. The shift smoothly approaches zero with the susceptibility. This result is insensitive to the details of the extrapolation of $\Delta H/\chi$ versus χ . Hence, with this modification of the original Hamiltonian, the measurements do predict a physically reasonable shift at high temperatures.

A plausible origin for this temperature-dependent hyperfine constant is contained in the following argument. Above 150K, there is a progressive decrease in the isotropic hyperfine field as shown in Figure 5. This corresponds to a decrease in s-like spin density at the phosphorus nucleus as the temperature increases. In the ground state, the partially occupied molecular orbitals of the phosphorus-ligand bonds are primarily hybridizations of the 3s, 3p, and probably some higher energy orbitals. Structural rearrangements such as bond bending, coiling, and length changes, which are common in polymeric materials, can be expected to modify the occupation of these orbitals. Thus there will be a temperature dependent behavior to the relative occupancy of the 3s and 3p orbitals on the phosphorus and therefore a similar behavior in the hyperfine interaction at the ^{31}P nucleus. Indeed, the magnitude of the effect observed in these studies (Fig. 5) is surprisingly large, suggesting that the orbital hybridization is a particularly strong function of the bond angles, which may in turn change with temperature.

The signal strength of the ^{31}P resonance did not increase with decreasing temperature as expected for a Curie-like system of weakly interacting nuclear moments. This suggests that the NMR spectral distribution is changing with decreasing temperature and therefore smaller numbers of ^{31}P nuclei contribute to the signal at lower temperatures. This is consistent with the existence of a distribution of exchange values.

SUMMARY AND CONCLUSIONS

The ^{31}P NMR of three structurally dissimilar materials with the same number of unpaired spins has been measured as a function of temperature. The degree of structural disorder so prominent in x-ray and optical studies appears only weakly in the observed line width. The line widths were analyzed to give an upper limit of approximately 0.1 percent for the amount of transferred spin density in the 3p orbital. The shift in field of the NMR was analyzed to give values ranging from 0.01 to 0.1 percent for the spin density in the 3s orbital. The lack of a Curie-law behavior to the intensity of the ^{31}P signal may indicate a redistribution of the spectral density associated with a broad distribution of superexchange interactions between magnetic ions.

Finally, further studies of this interesting class of magnetic materials must surely involve single crystal NMR studies to determine more accurately the relative spin densities in each of the orbitals on the phosphorus. This will in turn lead to a fuller understanding of the relative importance of such effects as bond bending on the distribution of exchange values.

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TABLE I

HYPERFINE EFFECTS IN THREE POLY(METAL PHOSPHINATES)

	<u>Cr A-type</u>	<u>Cr C-type</u>	<u>CDBP</u>
$H_{hf} = \frac{A}{g_e g_n \mu_n}$ (kOe)	2.8 ± 0.2	4.6 ± 0.1	3.4 ± 0.2
A (10^{-4} cm^{-1})	3.1 ± 0.2	5.1 ± 0.1	4.4 ± 0.2
$\frac{1}{2}$ 3S spin density	$0.09 \pm .01$	$0.14 \pm .02$	$0.11 \pm .01$
$\frac{1}{2}$ 3P spin density	2.0 ± 1	1.1 ± 0.2	0.3 ± 0.2

TABLE II

LINEWIDTH ESTIMATES FOR THREE POLY(METAL PHOSPHINATES)

	<u>Cr A-type</u>	<u>Cr C-type</u>	<u>CDBP</u>
ΔH (FWHM in Oe)	13.3 ± 0.1 (T = 300K)	10.3 ± 0.1 (T = 300K)	9.9 ± 0.1 (T = 300K)
	16.0 ± 0.2 (T = 125K)	12.6 ± 0.2 (T = 77K)	$10.5 \pm .1$ (T = 100K)

Figure Captions

- Figure 1 - Molecular structures for various poly(metal phosphinates), (a) is the structure for the Cr C-type, (b) denotes the Cr A-type (note the hydroxyl bridge) and (c) is the characteristic 1-3-1 scheme for the zinc and cobalt polymers (CDBP and the copolymer).
- Figure 2 - (a) The NMR signal of ^{31}P observed in the Cr C-type polymer at the output of the boxcar integrator. "f(H)" indicates the envelope of the signal.
(b) A plot of $\ln f(H)$ as a function of $(H-H_0)^2$. The straight dashed line is a theoretical Gaussian.
- Figure 3 - The paramagnetic shift of the ^{31}P NMR as a function of temperature for all three materials.
- Figure 4 - The paramagnetic shift of the ^{31}P NMR as a function of static magnetic susceptibility for all three magnetic polymers. The solid line is a theoretical extrapolation (see text).
- Figure 5 - The ratio of the paramagnetic shift divided by the static magnetic susceptibility plotted as a function of the magnetic susceptibility for the Cr C-type polymer. The straight line represents one possible extrapolation of the data.

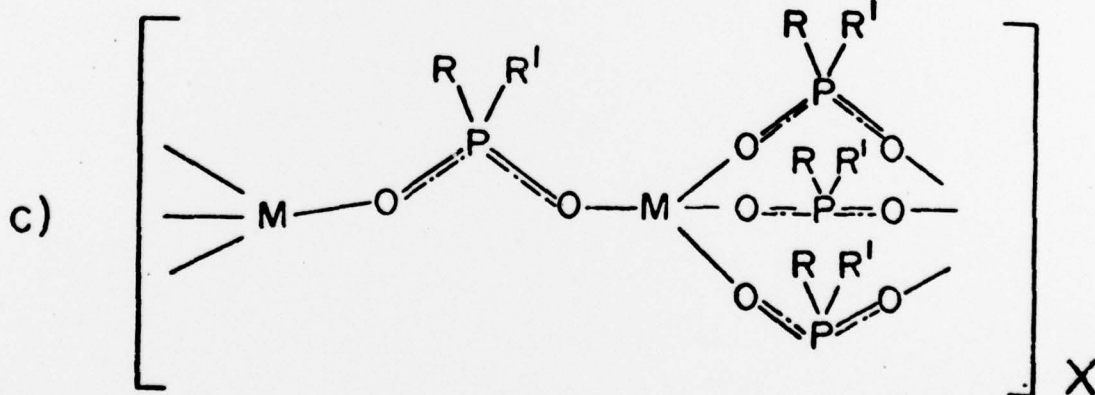
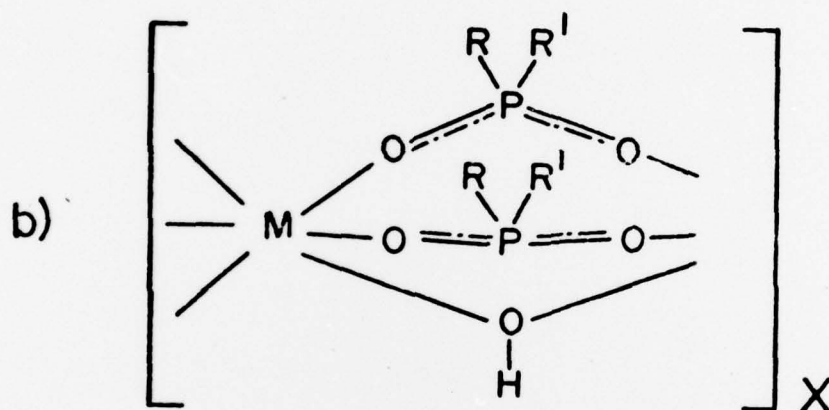
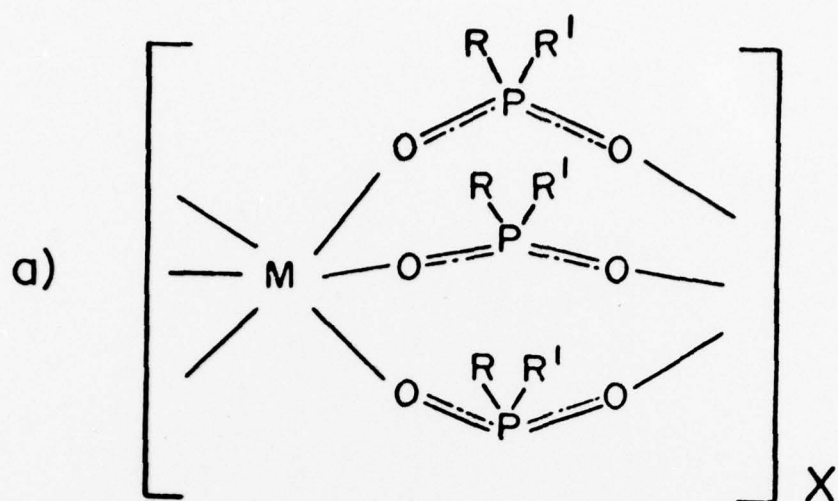


Figure 1

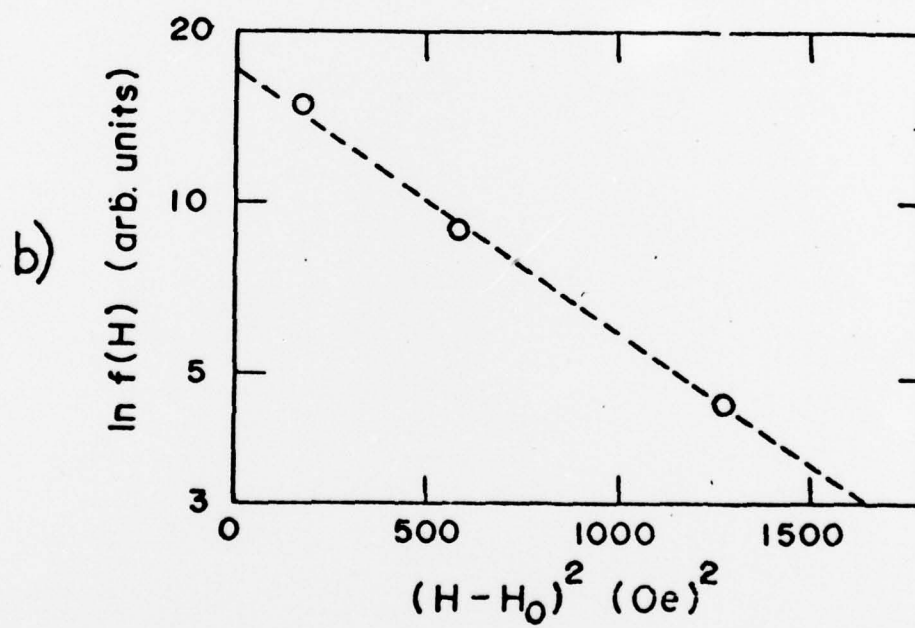
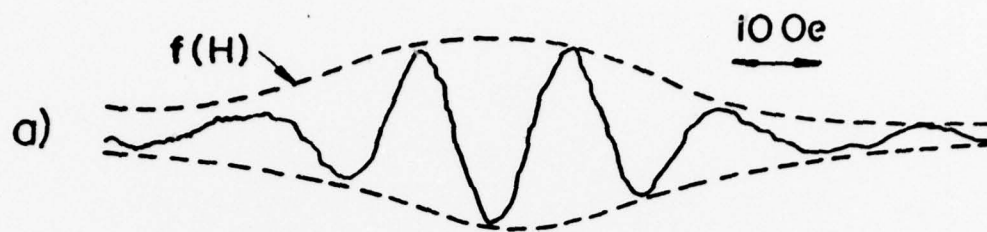


Figure 2

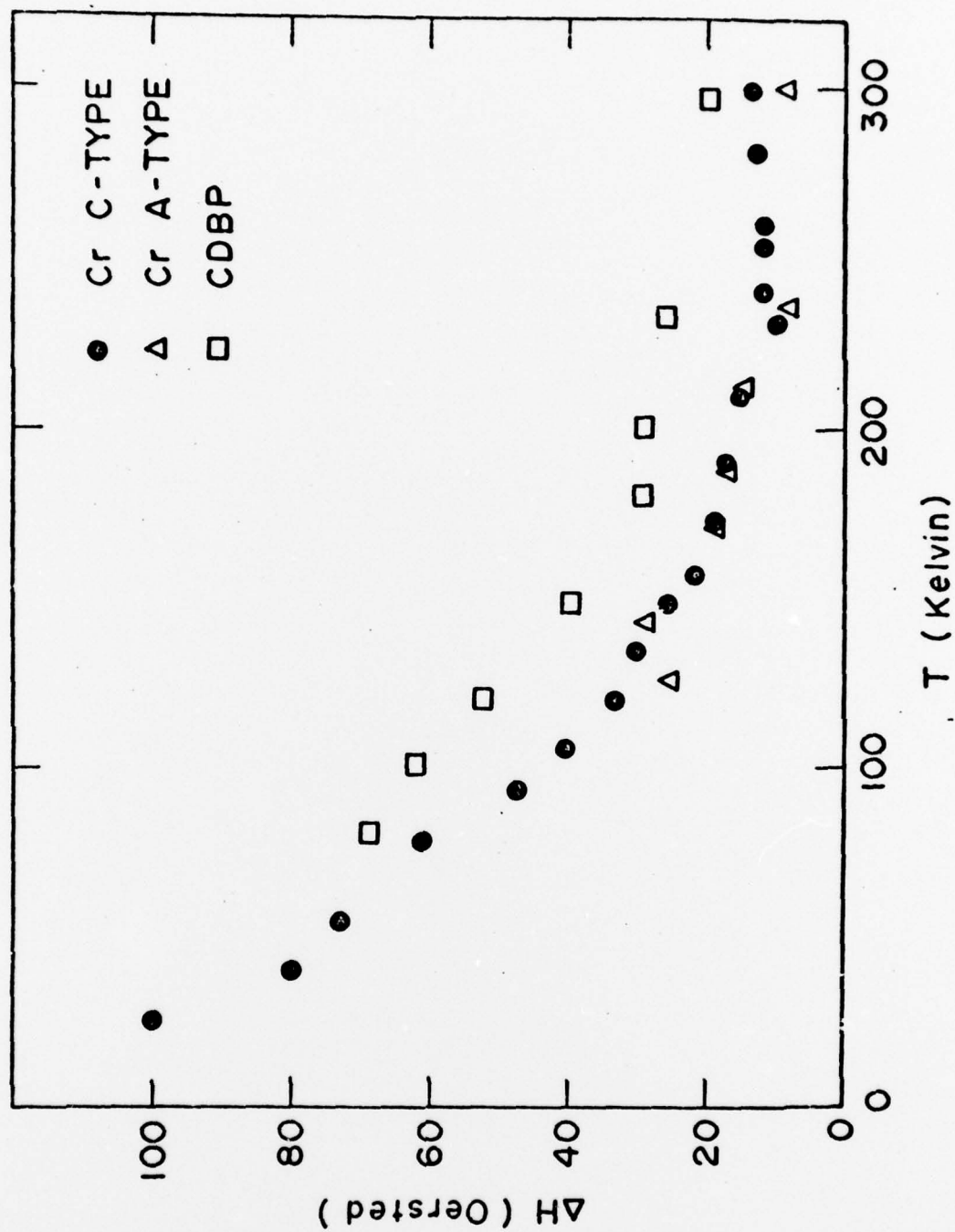


Figure 3

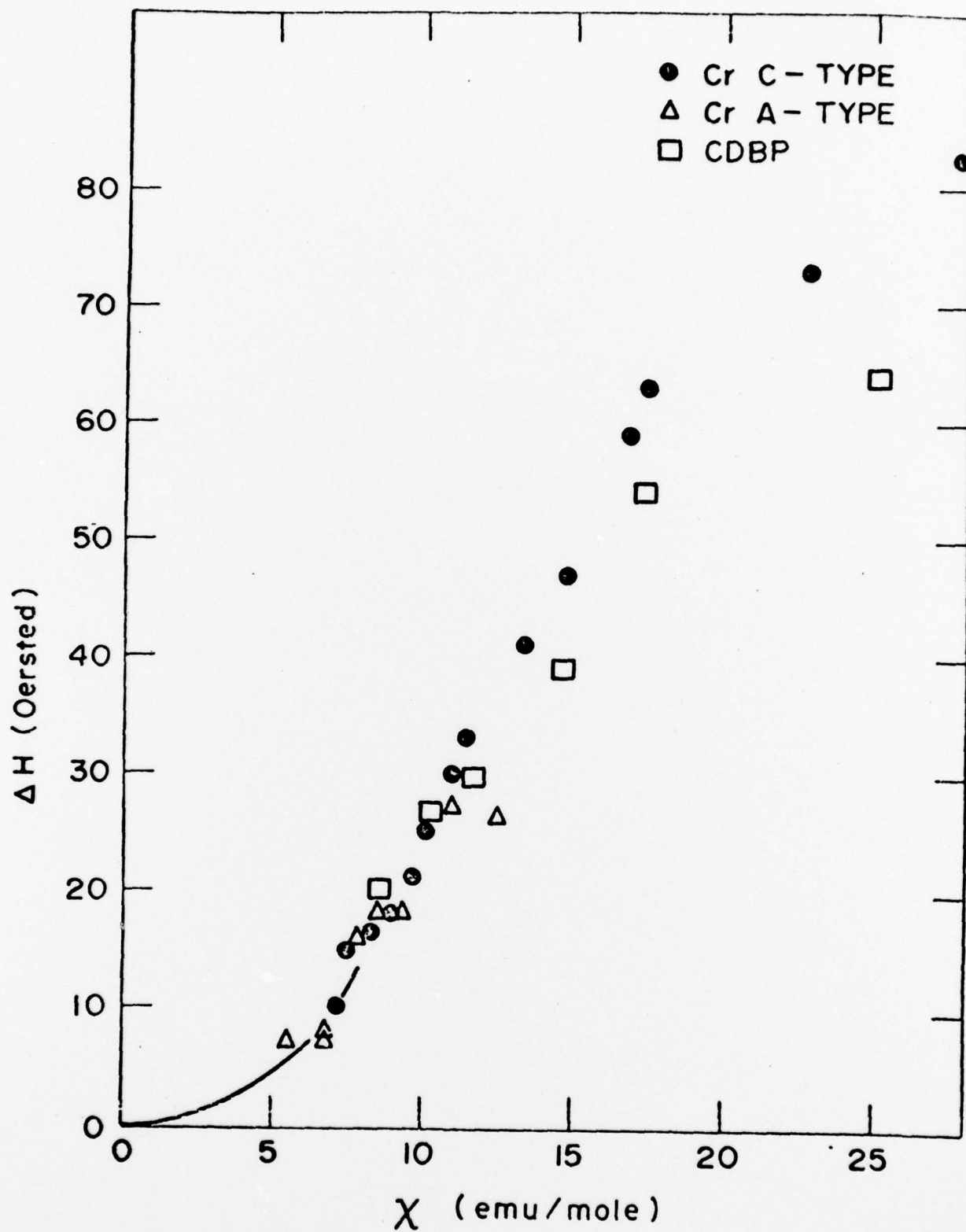


Figure 4

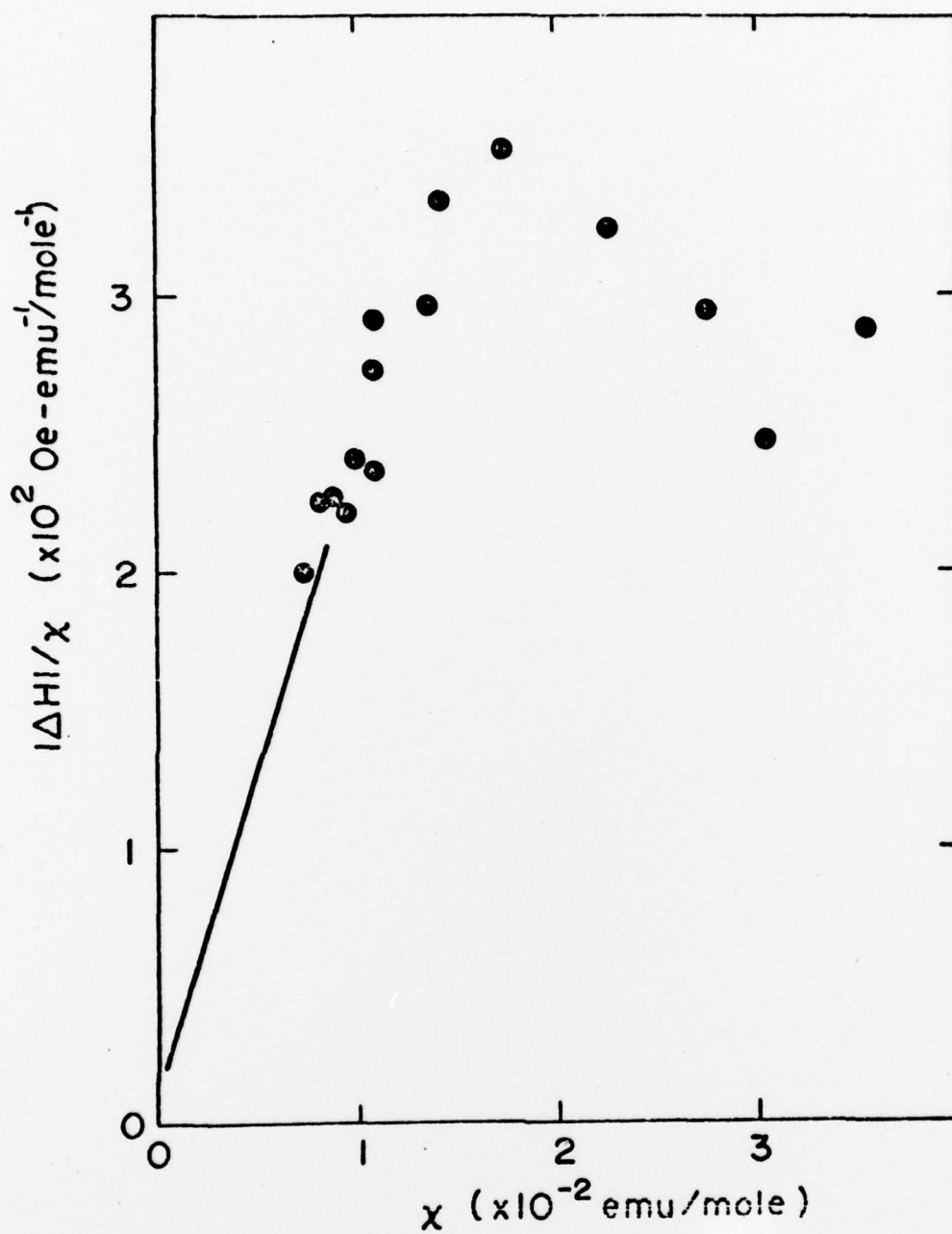


Figure 5

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The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D. C. 20350	1		
Commander, Naval Air Systems Command Department of the Navy Washington, D. C. 20360 Attn: Code 310C (H. Rosenwasser)	1		